

## Partial Ionic Bonding in Homogeneous Sodium Clusters

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In this work, we report an interesting observation of partial ionic bonding due to charge transfer in *homogeneous* sodium clusters. The charge transfer causes the electronic charge to accumulate on the surface, and the resulting charges on atoms range between  $+0.4$  to  $-1.0 |e^-|$ . We also demonstrate that this disparity among effective charges on atoms is geometry dependent, such that atoms experiencing similar surrounding, have equal effective charge. It is speculated that this phenomenon will occur among other homogeneous clusters as well, and its extent will be defined by the valence electron delocalization.

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## I. INTRODUCTION

Atomic clusters are interesting, useful, and intriguing.<sup>1-15</sup> Their finite size has brought out many counterintuitive observations about their various properties. For instance, bulk gold, which is a noble metal, acts as a catalyst in its cluster form. It is used as a chemical catalyst, as well as in biomedicine.<sup>3-5</sup> Bulk rhodium, which is a non-magnetic solid, turns magnetic in its cluster form.<sup>6</sup> Aluminum, which is usually used in its compound form as catalyst, shows catalytic activity when used as clusters.<sup>7,8</sup> Some clusters also exhibit higher than bulk melting temperature, which contradicts our understanding that melting temperature lowers with decreasing size.<sup>9-11</sup> All these odd properties of clusters are dependent upon the structure as well as their bonding. Bonding in clusters is quite different than their corresponding bulk material, and changes even across sizes of clusters of the same element. Gallium in its bulk form has metallic as well as covalent type bonding.<sup>12</sup> Bonding in its clusters, however has been an unresolved key issue.<sup>15-17</sup> Lead clusters are agreed to change their bonding from metallic to non-metallic, but the size at which this occurs, is still under debate.<sup>18-20</sup> Tin shows a semiconductor to metal transition with changing size of its clusters.<sup>21</sup> Thus, bonding among clusters has been a fairly debatable issue for clusters of many elements, and is a key factor in understanding and explaining their behavior. Amidst all these controversies, bonding in sodium clusters has come clean till now. Sodium clusters have been shown to possess metallic bonding.<sup>13,22-24</sup> In this work, we show that bonding in sodium clusters is more than just metallic, using atomic charge measurements. Charge transfer in heterogeneous systems is a known fact, where the amount of charge that gets transferred, depends upon the electron affinities of corresponding elements. In this work, we present an evidence of substantial charge transfer observed in *homogeneous* clusters of sodium. Such charge transfer is known to occur, in small quantities, in a few homogeneous clusters.<sup>8,25,26</sup> However, to the best of our knowledge, its extent and its influence on bonding have not been studied to date.

In what follows, we discuss the charge distribution of homogeneous sodium clusters with sizes up to few hundred atoms. We present Bader charge analysis of sodium clusters with sizes ranging from few 10 to few 100 atoms. Specifically, we demonstrate that in neutral sodium clusters, most of the atoms either gain or lose charge, and that the excess charge on each atom varies from  $+0.4$  to  $-1.0$   $|e^-|$ . Thus, in a cluster, some atoms are positively charged, while some others possess an effective -ve charge. This gives rise to a somewhat

counterintuitive phenomenon of partial ionic bonding among homogeneous clusters of sodium atoms. As a result of the charge transfer, electronic charge is observed to accumulate on the surface of the cluster and towards center. Geometry plays a crucial role and atoms with identical environment have identical effective charge. In case of highly symmetric clusters, like 55 and 147, we observe that atoms belonging to the same shell have identical charge polarity. Charge difference is more for geometries that are symmetric and ordered. By ‘ordered’, we mean geometries with more number of atoms experiencing similar environment, in terms of neighboring atoms. Although it is possible to infer and correlate our observations with polarizability and electric dipole moment, it should be noted that the focus of this work is upon bringing out the interesting observation about structure induced inhomogeneity of charge distribution in homogeneous sodium clusters. The article is organized as follows. Section II outlines the computational details, and section III, the results and discussions. Conclusions are drawn in section IV.

## II. COMPUTATIONAL DETAILS

Ab initio molecular dynamics is carried out within the Kohn-Sham formulation of density functional theory (DFT). Projector Augmented Wave pseudopotential<sup>27,28</sup> is used, with Perdew Burke Ehrzenhof (PBE)<sup>29</sup> approximation for the exchange-correlation and generalized gradient<sup>30</sup> approximation, as implemented in plane wave code, Vienna Ab initio Simulation Package (VASP).<sup>31–33</sup> Energy cutoff for plane-waves is kept at 102 eV for finite temperature molecular dynamics. Relaxation runs are carried with high precision setting in the VASP package, raising the effective energy cutoff to 127 eV. Cubic simulation cell, with image in each cell separated by at least 10 Å, is used. Energy convergence criterion of  $10^{-5}$  eV, and a force cutoff of 0.001 eV/Å are used for relaxation. The geometries used in this work are obtained from the authors of previous works,<sup>34</sup> and 309 and 561 icosahedra are taken from the Cambridge Cluster Database.<sup>35</sup> All the geometries used in this work are relaxed within defined computational accuracy, at the level of theory used here.

We have carried out Bader charge analysis for sodium clusters of numerous sizes ranging from 10-80, intermittent sizes up to 147, and larger icosahedral clusters with 309 and 561 atoms. Bader charge analysis was chosen on account of its reliability in comparison with other methods like Mulliken, Hirshfeld, that are used to calculate atomic charges.<sup>36–39</sup> Bader

analysis makes use of the fact, that in molecular systems, the charge density between atoms reaches a minimum. The point of minimum charge density is used to separate atoms from each other. This analysis defines atoms using a 2-D surface, on which the charge density is a minimum, perpendicular to the surface. The charge enclosed within the Bader volume is a good approximation to the total electronic charge of an atom.<sup>40-42</sup> In order to be able to reproduce total charge on system correctly, fine meshes are used for Bader charge calculations. The same fine FFT meshes are used for computing wavefunctions and charges during relaxation. We make use of 2-D mapping of atoms, described below, to analyze the occurring redistribution of charges.

### A. 2-D mapping of atoms

In order to quantify the effective charge on each atom as a function of its position, each atom is mapped onto the 2-D plane and is colored according to the charge it possesses. For this mapping, we plot the perpendicular distance of each atom from the three axes,  $x$ ,  $y$ , and  $z$ , against the  $x$ ,  $y$  and  $z$  coordinate of that atom. For better graphical representation, the distance of each atom from  $x$ ,  $y$  and  $z$  axes is given the arithmetical sign of  $y$ ,  $z$  and  $x$  coordinate of that atom. Such a representation of atoms from 3-D to 2-D is most useful, when dealing with spherical geometries. It helps bringing out the shells in spherical geometries, whenever present. Each point on this 2-D graph represents an atom, and is colored according to the charge it possesses.

### B. Charge measuring convention

Charge on each atom is measured in excess of 1 valence electronic charge of a neutral Na atom. Schematics of the convention are shown in Fig. 1. For instance, any atom with charge greater than  $1.0 |e^-|$ , is given a -ve sign (since it has accumulated -ve charge), and a magnitude in units of ‘excess of  $1.0 |e^-|$ ’. The charge polarity is also defined based on the same scale. For example, any atom gaining  $0.4 |e^-|$  excess electronic charge is said to have a  $-0.4 |e^-|$  charge, while an atom loosing  $0.4 |e^-|$  electronic charge, is said to possess  $+0.6 |e^-|$  charge.

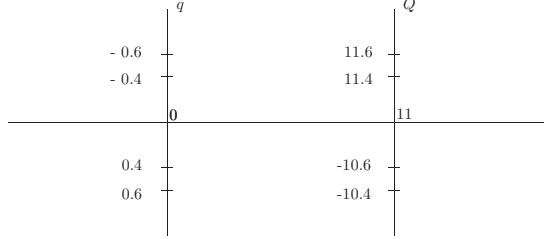


FIG. 1. Diagram showing the convention of measuring effective charge used in this work, in comparison with the total charge on sodium atom.  $q$  : Effective charge on sodium atom as measured in this work.  $Q$  : Actual charge on sodium atom.

### C. Shape parameter

Shape parameter  $\varepsilon_{\text{def}}$  is used to quantify the distribution of atoms along the three spatial directions.<sup>43</sup> It is a rough measure to quantify the overall shape of the cluster. It is defined as:

$$\varepsilon_{\text{def}} = \frac{2Q_x}{Q_y + Q_z},$$

where,  $Q_x \geq Q_y \geq Q_z$  are the eigenvalues of the quadrupole tensor defined as  $Q_{ij} = \sum_I R_{Ii} R_{Ij}$ .  $R_{Ii}$  stands for the  $i^{\text{th}}$  coordinate of ion  $I$ , measured from the origin. The structure is prolate, when  $Q_x \gg Q_y \approx Q_z$ . For a spherical geometry,  $Q_x = Q_y = Q_z$ , and  $\varepsilon_{\text{def}} = 1$ .

## III. RESULTS AND DISCUSSION

We begin our results and discussion by presenting 2-D mappings of atoms, colored by magnitude of effective charge on each atom, for various sizes, in Fig. 2. Cluster geometries for these sizes, are shown in Ref.<sup>44</sup>. The sizes of clusters are mentioned at the top right of each frame. The axes in the graph represent the position of each atom with respect to center of mass (COM), in 2-D mapping. The first two figures are for sizes 55 and 147. Both these structures are Mackay icosahedra. In these structures, -ve charge clearly gathers on the surface, and on the central atom. These two clusters comprise of atoms arranged in concentric shells, and as seen from the figure, charge on atoms that belong to the same shell has same polarity and hardly varies in magnitude. This is attributed to the fact that atoms in the same shell confront identical environment. Same is further demonstrated in geometries

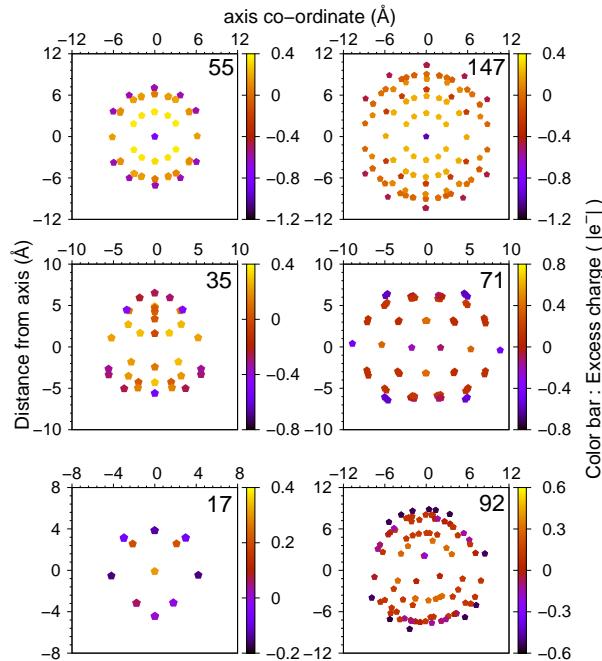


FIG. 2. Charge distribution for various Na clusters. Electronic charge accumulates on the surface of all these clusters. Atoms at center also accumulate -ve charge, except that of 17. Spatial symmetry of clusters gets reflected in charge distribution.

35 and 71. These two geometries are not concentric shells, but have local order. 35 has three centers of local order, and that shows up here as three different sets of atoms possessing identical charge distribution. Similarly, 71 is a structure formed by two intermeshing size 55 icosahedra with two centers of local order. Owing to this two centered local order, we expect a two centered charge distribution. The graph for size 71 does show two innermost atoms possessing high electronic charge (dark shade). This is in line with the fact that electronic charge prefers to accumulate towards the center of cluster. Size 17 is the smallest size with structure that encloses a sodium atom. It exhibits a different behavior than other sizes, which is due to its small size. Particularly, its central atom has effective +ve charge, in contrast with other sodium clusters. Its surface has an overall -ve charge, with 10 out of 16 atoms charged -ve, four charged +ve, and the rest neutral. The last frame in the figure is for size 92. The ground state (GS) for this size is reported to possess a non-icosahedral local order,<sup>45</sup> which is reflected in the charge distribution shown here. The four atoms at the innermost shell have almost identical charge. Also, with a couple of exceptions, all other atoms in their respective shells have little or no variation in magnitude of charge that they

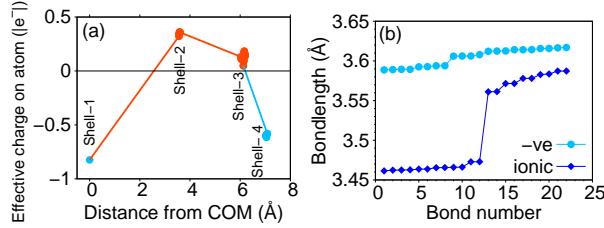


FIG. 3. Analyses for  $\text{Na}_{55}$ : (a) All atoms in a given shell have same charge polarity. (b) First 22 shortest bonds in  $\text{Na}_{55}$  are between atoms with opposite polarity (dark blue). Shortest bondlengths between atoms with -ve polarity are shown in light blue.

posses (maximum variation in magnitude of charges in same shell is  $\sim 0.03 |e^-|$ ). This can be attributed to the local order that 92 possesses. Thus, we demonstrate that various different geometries of sodium clusters show the common trait that free standing sodium clusters possess a -vely charged surface, with ‘effective charge on an atom’ being a function of its neighborhood.

Charge transfer among atoms of  $\text{Na}_{55}$  is further investigated in detail. A 55 atom icosahedron consists of 4 concentric shells with 1, 12, 30 and 12 atoms. Fig. 3(a) shows the effective charge on each atom, plotted against its distance from center of mass (DCOM). Atoms that gain electronic charge, are colored blue, while those that loose electronic charge, are colored orange in the plot. We see from the figure that atom at the COM gathers an excess of  $0.8 |e^-|$  electronic charge, while all atoms in the second shell ( $\text{DCOM}=3.61 \text{ \AA}$ ) loose about  $0.4 |e^-|$  electronic charge each. Similarly, atoms in the third shell loose electronic charge and the outermost shell atoms gain it. The collective magnitude of this charge transfer is quite large for the entire shell of atoms. There is a change of charge polarity accompanied by a nearly  $11 |e^-|$  cumulative charge difference, between the third and the fourth shell, as well as between second and the fourth shell. Hence, we speculate that this transfer of charge among the shells leads to an ionic contribution to the stability of bonds formed between atoms of these shells. Further analysis of bondlengths confirms this speculation. It shows that the shortest bonds are formed between atoms of the 4<sup>th</sup> and the 2<sup>nd</sup> shell. This indicates that the shortest bonds in this cluster posses an ionic character to it, owing to disparity of charges on respective atoms. Plotting the bondlengths of atoms of same polarity, and opposite polarity, shows that the set of first 22 shortest bonds are those formed between atoms with opposite polarity, as shown in Fig. 3(b). This comparison was also made for all 107 different sizes

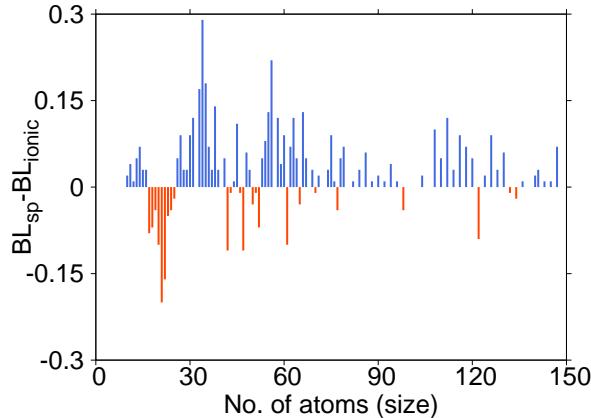


FIG. 4. Plot of difference between the shortest ionic bondlengths, and the shortest bondlengths of atoms with same polarity, plotted against the size of the cluster. The shortest bonds are between atoms with opposite polarity for most of the sizes.

between 10-147. It revealed that 84 out of these 107 sizes had their shortest bond formed between atoms with opposite polarity (ionic). Fig. 4 shows the plot of difference between the shortest bond between atoms with same polarities ( $BL_{sp}$ ) and the shortest bond between atoms with opposite polarities ( $BL_{ionic}$ ). The difference is positive whenever the shortest bond is ionic, and negative otherwise. As seen from the figure, most of the sizes show this difference to be positive, which implies their shortest bonds are between atoms with opposite polarity. This clearly demonstrates the overall influence of ionic character on bonding in sodium clusters, and that the ionic contribution to bonding in sodium clusters cannot be overlooked within this size range.

Next, we compare observations noted for  $Na_{55}$ , with higher sized icosahedra. As shown in Fig. 5, with increasing number of atoms in each shell, polarity of effective charge on each atom in a given shell does not remain same. Fig. 5(a) consists of the 2-D mapping of atoms for size 561. The points on this graph are colored by polarity of effective charge on each atom, and not their magnitude. Atoms that gain electronic charge, are colored blue, while those that loose electronic charge are colored orange. The figure makes it clear that there is an electronic charge accumulated towards center and on the surface. Also, the uniform charge polarity and magnitude among all atoms in same shell, previously seen in  $Na_{55}$ , is absent here. This is shown in Fig. 5(b), in which magnitude of charge transfer on each atom is plotted as a function of the respective DCOM. We also note that variation in effective charge on each atom in a given shell, is more compared to smaller icosahedra.

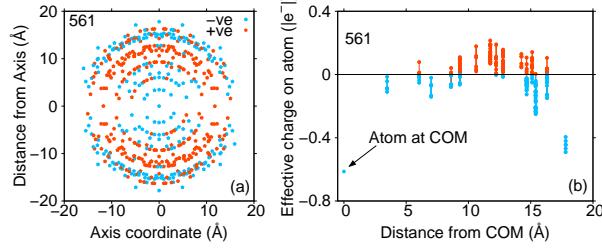


FIG. 5. (a) Distribution of charge polarities of atoms in each shell of Na<sub>561</sub>. (b) Charge on each atom as a function of its distance from center of mass for Na<sub>561</sub>. For larger sizes, atoms in same shell do not posses identical charge polarity. Also, the variation in charge magnitudes is greater in each shell, in comparison with smaller icosahedra.

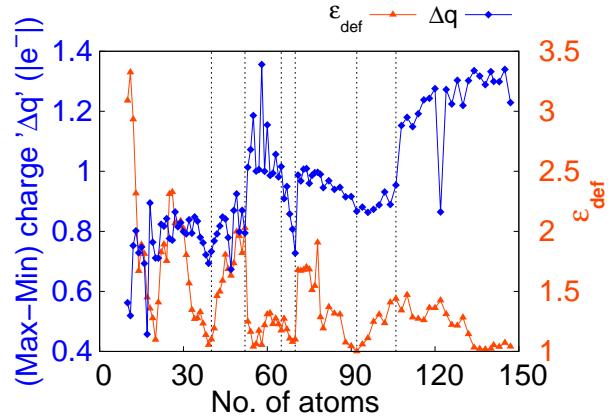


FIG. 6. Difference between maximum and minimum charge on an atom in cluster ( $\Delta q$ ), as a function of size of the cluster. Right  $y$ -axis shows variation in shape parameter ( $\varepsilon_{\text{def}}$ ).  $\Delta q$  follows the changes in geometrical motifs closely.

Similar analyses for size 147 and 309 atom icosahedra, are presented in Ref.<sup>44</sup>. Although 147 icosahedron follows same trends as that of 55, 309 icosahedron marks the beginning of trends observed in 561.

While the effective charge on atoms should show no variation for sodium bulk, it is interesting to study the same for clusters, as a function of their size and shape. Hence, variation of the ‘difference between maximum and minimum effective charge on an atom in a cluster’ ( $\Delta q$ ) is studied as a function of size of the cluster. Fig. 6 shows a plot  $\Delta q$  as a function of size of the cluster. Shape deformation parameter  $\varepsilon_{\text{def}}$  is plotted on the right  $y$ -axis of graph. The figure shows that  $\Delta q$  is maximum whenever the geometry assumes icosahedral motif. Sodium clusters show globally disordered structures with local

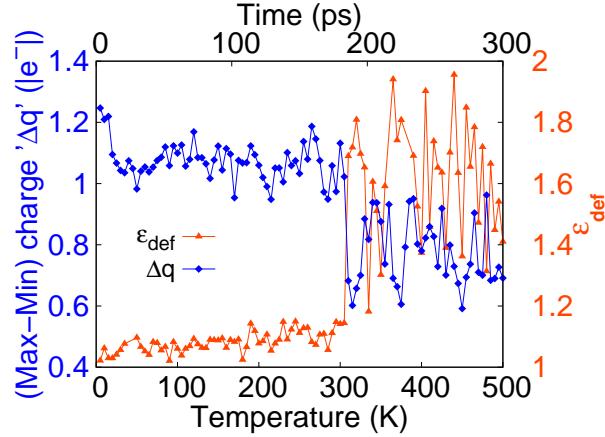


FIG. 7.  $\Delta q$  for 100 different geometries sampling a heating run of  $\text{Na}_{55}$  between 0-500 K. Right  $y$ -axis is the corresponding variation in shape parameter ( $\varepsilon_{\text{def}}$ ). Out of phase variation in  $\Delta q$  and  $\varepsilon_{\text{def}}$  signifies  $\Delta q$ 's preference for spherical geometries.

icosahedral order starting from size 19 intermittently till 52. A sudden change in motif occurs from 52 to 53. Icosahedral order is then followed for sizes 53 to 64.  $\Delta q$  also shows the sudden jump from 52 to 53, and has high value till size 64. The ground state structures are disordered between 64 and 70, and  $\Delta q$  also shows a dip in its value in this size range. Change of motif from one centered to two centered icosahedra is indicated by sudden rise in  $\varepsilon_{\text{def}}$  at 70.  $\Delta q$  mimics the same, and goes hand in hand with this change of motif. Clusters become more disordered with less icosahedron like structure till 92 and up to 106, gradually.  $\Delta q$  also lowers in value gradually between 71 through 92 and up to 106. While value of  $\varepsilon_{\text{def}}$  is very close to 1 around size 90, the order is not icosahedral. This correlates well with observed variation in  $\Delta q$ . After size 106, the geometrical order regains the icosahedral motif, which builds up and completes the next icosahedron at 147. Similar growth trend is followed by  $\Delta q$  as well. Sudden drop in  $\Delta q$  at size 122 is due to abrupt displacement of its atom nearest to COM at  $2.5\text{\AA}$ , in comparison with its neighboring sizes, who have nearest atom from their COM at  $1.5\text{\AA}$ . Thus, we see that  $\Delta q$  follows the growth pattern of sodium clusters closely, and maximizes whenever the geometries have icosahedral motif. For larger sizes 309 and 561,  $\Delta q$  has lower values ( $1.24$  and  $0.82 \text{ } |e^-|$ ), which points to the fact that as the system goes on becoming larger, this quantity dies out. It will reach the value of zero for infinite solid bulk sodium. This is in agreement with our understanding that in solid bulk, all sodium atoms should possess identical charge, on account of the identical surrounding of each of them.

Next, we investigate the effect of temperature on charge transfer as observed in  $\text{Na}_{55}$ . Towards this end, we have performed slow-heating of  $\text{Na}_{55}$ . MD run was started with initial geometry as the icosahedron. 100 different geometries are picked out of this heating run carried out between 0 to 500 K, in 300 ps. The sampling is done in an unbiased way, by picking out a geometry every 3 ps. Bader analysis is performed for these unrelaxed geometries in order to investigate charge redistribution at finite temperature. Fig. 7 is a graph of  $\Delta q$  for these geometries. In this figure, temperature is plotted on  $x$  axis, and the simulation time on upper  $x$ -axis. Right  $y$ -axis shows the corresponding variation in shape parameter ( $\varepsilon_{def}$ ). Value of  $\Delta q$  is the highest in the graph initially, when the geometry is a perfect icosahedron. It drops initially, as the cluster changes shape due to increased temperature, as atoms begin to vibrate about the ideal icosahedron positions.  $\Delta q$  values oscillate about  $1.05 |e^-|$  during the phase when cluster is distorted, before it actually melts.  $\Delta q$  suffers another drop upon melting of cluster, and even after melting, it attains higher values whenever the cluster becomes spherical. In this figure, high values of  $\Delta q$  occur at points when  $\varepsilon_{def}$  shows a low value (close to 1). This implies that  $\Delta q$  is large for spherical geometries, and has lower values otherwise.

Based on all the analyzes mentioned above, we have brought out a simple, yet counter-intuitive and interesting picture of bonding in homogeneous sodium clusters. Indeed, it is an artifact of the finite size of the system. In sodium bulk, all the atoms witness identical environment, and there is no reason for its the delocalized electrons to favor certain atomic sites in preference over the others. All atomic sites in the infinite solid are equivalent in terms of their neighboring environment. In contrast to this, in a finite sized system, most atoms hold unique positions in terms of their neighboring environment, along with existence of certain equivalent positions, that are decided by the symmetry of the cluster. Atoms at the distinct positions have distinct effective charge, while atoms experiencing identical environment possess identical effective charge. An interesting manifestation of this is seen in icosahedral structures for various sizes from 55 to 561. Thus, all atoms do not experience equivalent environment in a cluster, which results into partial ionic bonding in these clusters. Hence, we see that this counterintuitive phenomenon of partial ionic bonding among a finite collection of homogeneous atoms, is an artifact of the finite size of the system, and should be expected to occur among all finite sized system to a varied degree.

## IV. CONCLUSIONS

We have demonstrated that charge transfer occurs in homogeneous sodium clusters, which gives rise to ionic character in bonding. Charge tends to accumulate onto the surface of these clusters, and towards their center. Magnitude of effective charges depends on the size as well as symmetry of the cluster. The effect is most prominent for clusters with few 10s to few 100s of atoms. The charge difference between atoms is more for more symmetric clusters. Since the charge transfer observed here is geometry and symmetry dependent, one may expect this phenomenon to occur in homogeneous clusters of other elements as well, in varying magnitudes.

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